DARPA Perspectives on Multifunctional Materials/Power and Energy

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What makes DARPA unique…

Formed in 1958 to
PREVENT and **CREATE** strategic surprise

Capabilities, mission focused

Finite duration projects

Diverse performers

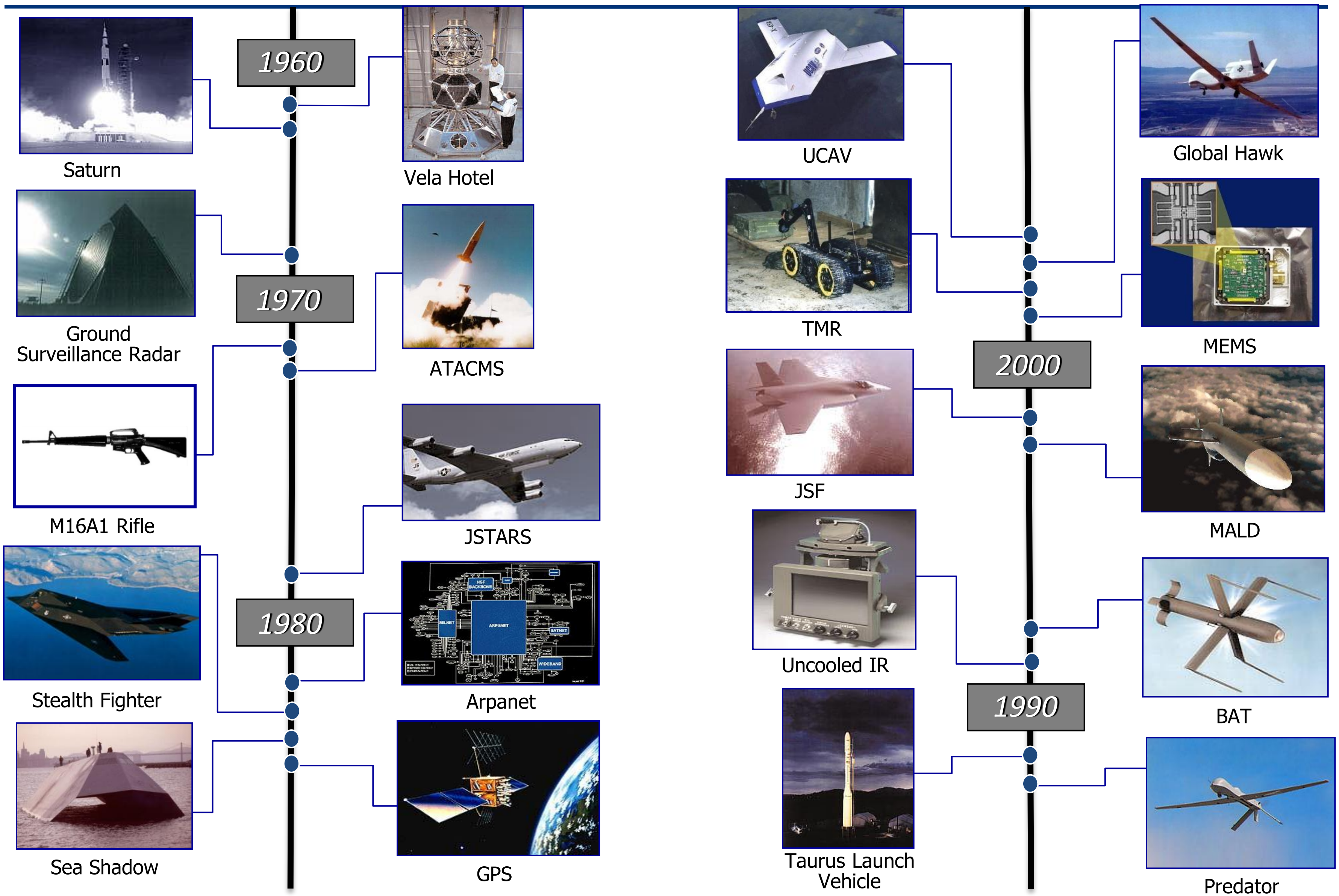
Multi-disciplinary approach…from
basic research to system engineering

As the DoD's innovation engine, we
are committed to the boldest, creative leaps…

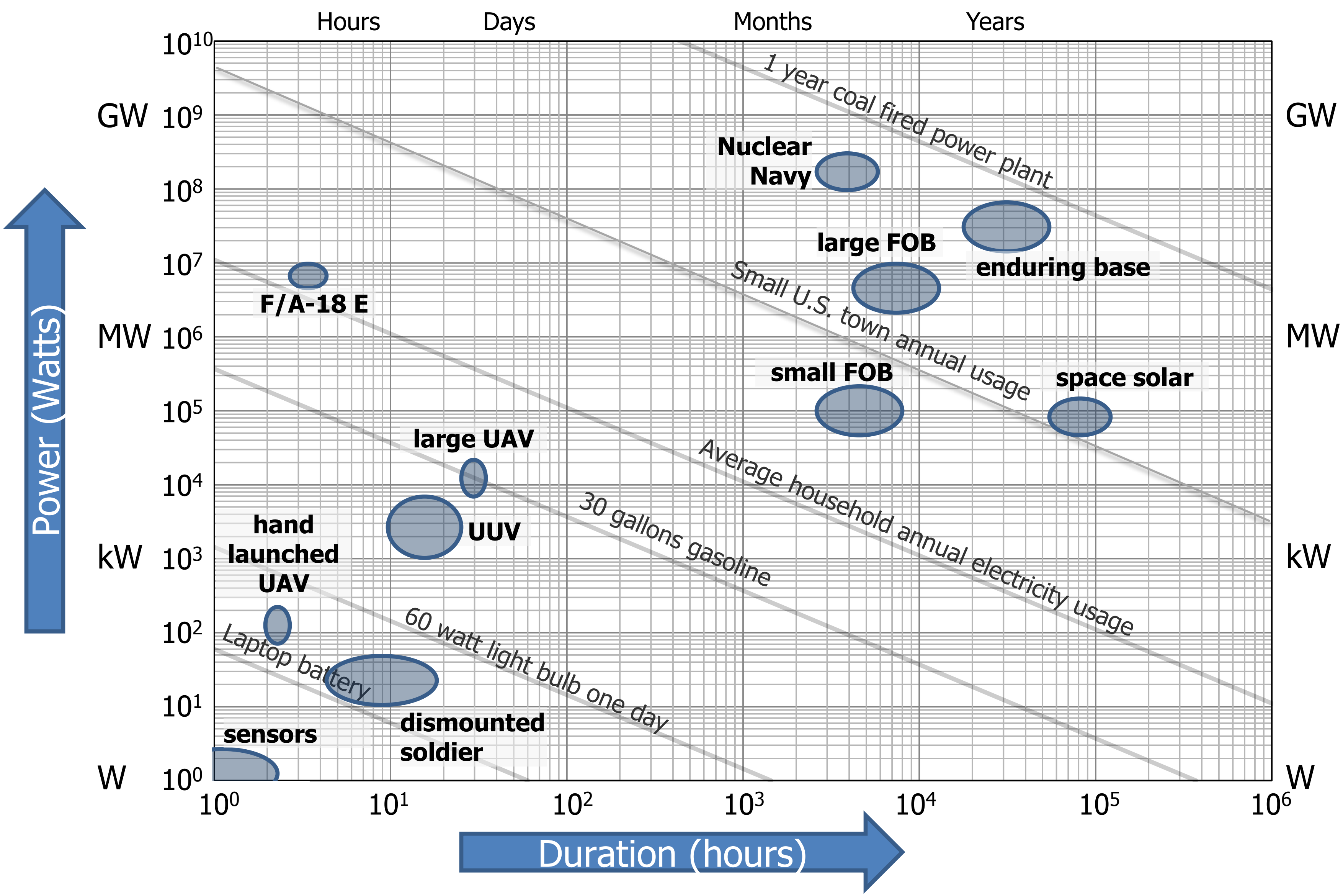
DARPA's Current Office Structure

DSO	MTO	I2O	TTO	STO	AEO
Physical Sciences	Basic Science Core	Global ISR	Advanced Weapon Systems	Comms, Networks & Cyber	Agile Programs with Frequent Development Cycles
Materials	Devices	Cyber	Advanced Platforms	Global Tactical ISR	Conduct Systematic Rigorous Assessments
Mathematics	Integration	Social Networks		Hybrid Warfare	Explore New Contracting Approaches
Training & Human Effectiveness	Power	Computational Social Science		Extreme Environments	Develop Strong Relationships
Biological Warfare Defense	Architectures	Language Transparency			
Biology	Application	Edge Finding			
		Training/ Education			
Defense Sciences Office	**Microsystems Technology Office**	**Information Innovation Office**	**Tactical Technology Office**	**Strategic Technology Office**	**Adaptive Execution Office**

DARPA accomplishments



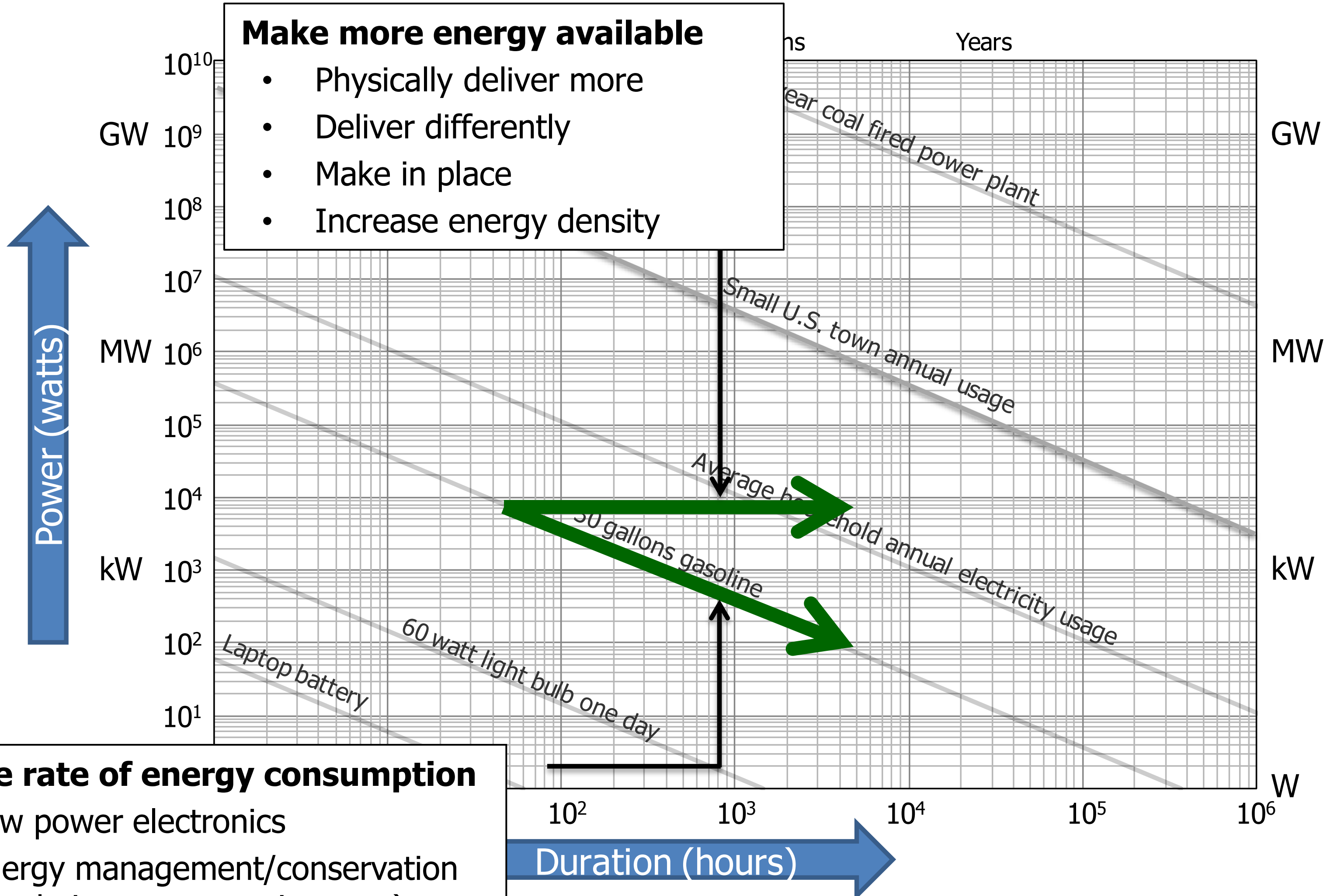
Energy usage for DoD missions covers many orders of magnitude



Two approaches to the DoD energy challenge

Make more energy available

- Physically deliver more
- Deliver differently
- Make in place
- Increase energy density

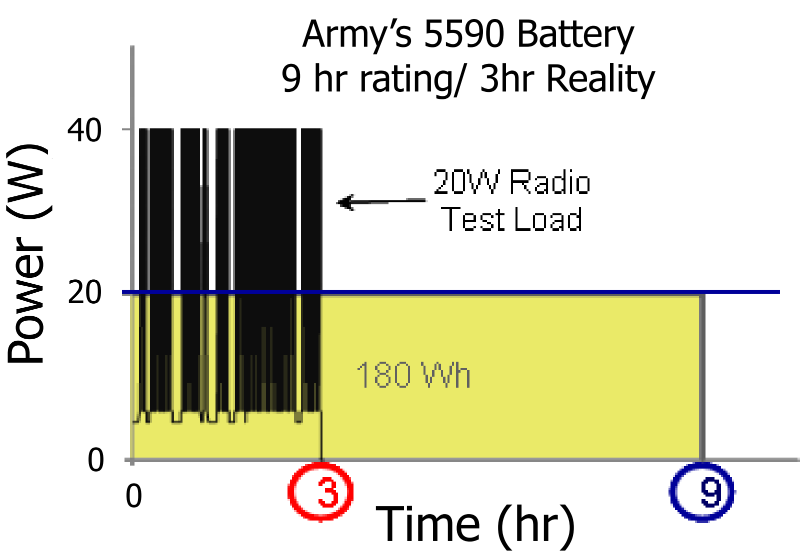


Reduce rate of energy consumption

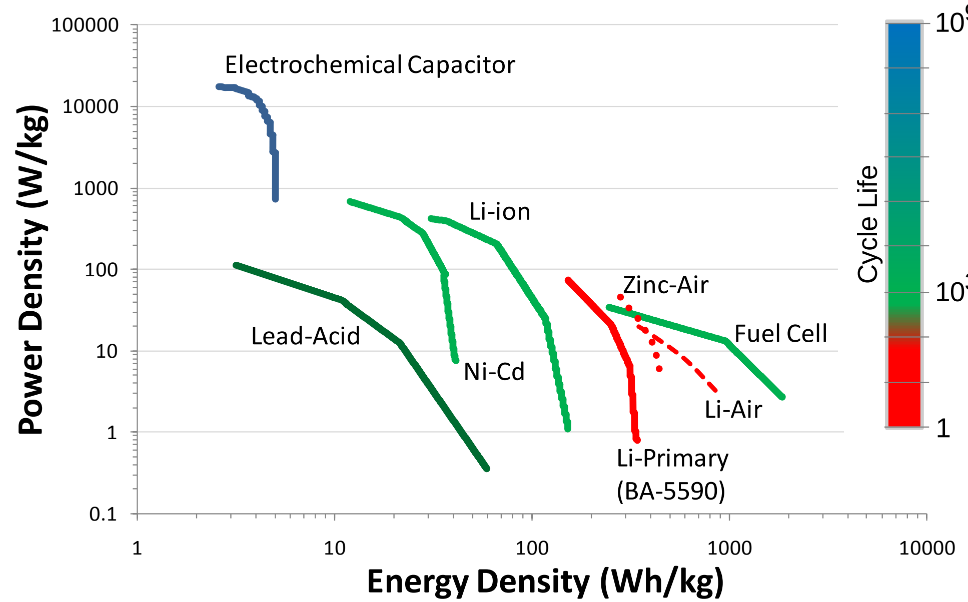
- Low power electronics
- Energy management/conservation (insulation, cogeneration, etc.)

Increased energy density: Hybrid energy components and systems or enhanced batteries

GOAL: Portable energy sources that support transient power loads without the energy extraction inefficiencies associated with batteries.



Current DoD batteries fail to deliver full energy content under transient power demands.



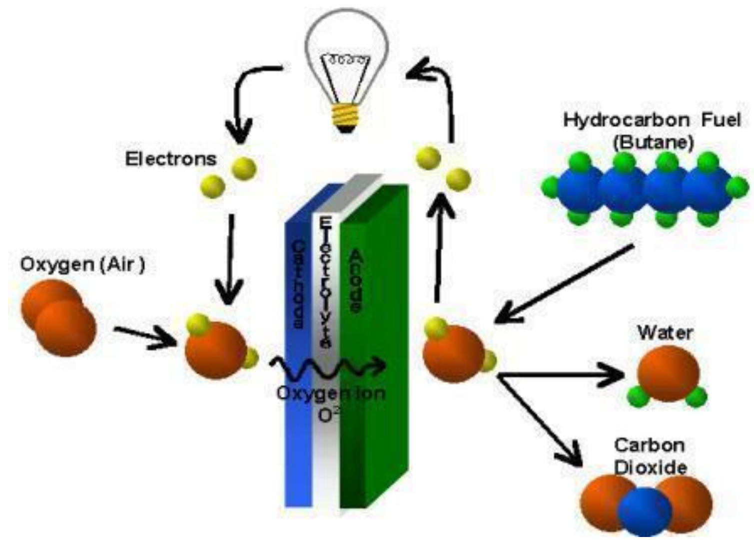
Development of innate and discrete hybrid systems combined with smart power management circuits.

3x increase in the runtime over SOA batteries.

- Minimize energy losses to power spikes (*e.g.*, high power transmission on portable radios).
- Enable safe operation of high energy density batteries without thermal runaway.
- Lighten battery burden on dismounted soldier.
- Lengthen operation time of unmanned systems.
- Improve safety through peak-load mitigation.

Dramatically increased energy density: Compact solid oxide fuel cell

Solid Oxide Fuel Cell (SOFC) electrochemically oxidizes energetically dense fuel (propane or butane) for power from a non-combustion path.



Propane SOFC:

- High energy density (>4x longer duration than battery power for UAV mission).
  - 20% efficiency on propane fuel provides up to 2000 Wh/kg, improving with longer missions:
    - 8 hour UAV mission: ~600 Wh/kg.
    - 24 hour mission: ~1200 Wh/kg.
    - 72 hour mission: ~1800 Wh/kg.
- Current technology requires propane (or butane) with less than 50 ppm sulfur.
  - Worldwide availability.
  - Can clean through disposable carbon filter.

Extended duration with liquid fuels: DARPA's Stalker XE240 Unmanned Aerial Vehicle (UAV)

GOALS: Developed deployable, ruggedized fuel cell/airframe to survive multiple landings.

Meet user need for 6+ hr flight endurance. (The state of art is a <2.5 hr, single-payload mission with a Li-ion battery.)

ACHIEVEMENTS:

DARPA performer met or exceeded milestones to demonstrate:

- 8+ hour duration (testing included two 6-hr flights, one 7-hr flight, and one 8-hr flight).
- 14 flights/landings on same air frame and fuel cell (goal was 10 flights/landings).
- High altitude launch (7,500 ft. density altitude) and flight (>15,000 ft. density altitude).
- Adverse weather flight (high winds with >30 mph gusts and rain).
- Rapid turnaround between landing and re-launch (<30 min).
- Day/night flight.
- Cold start capability.

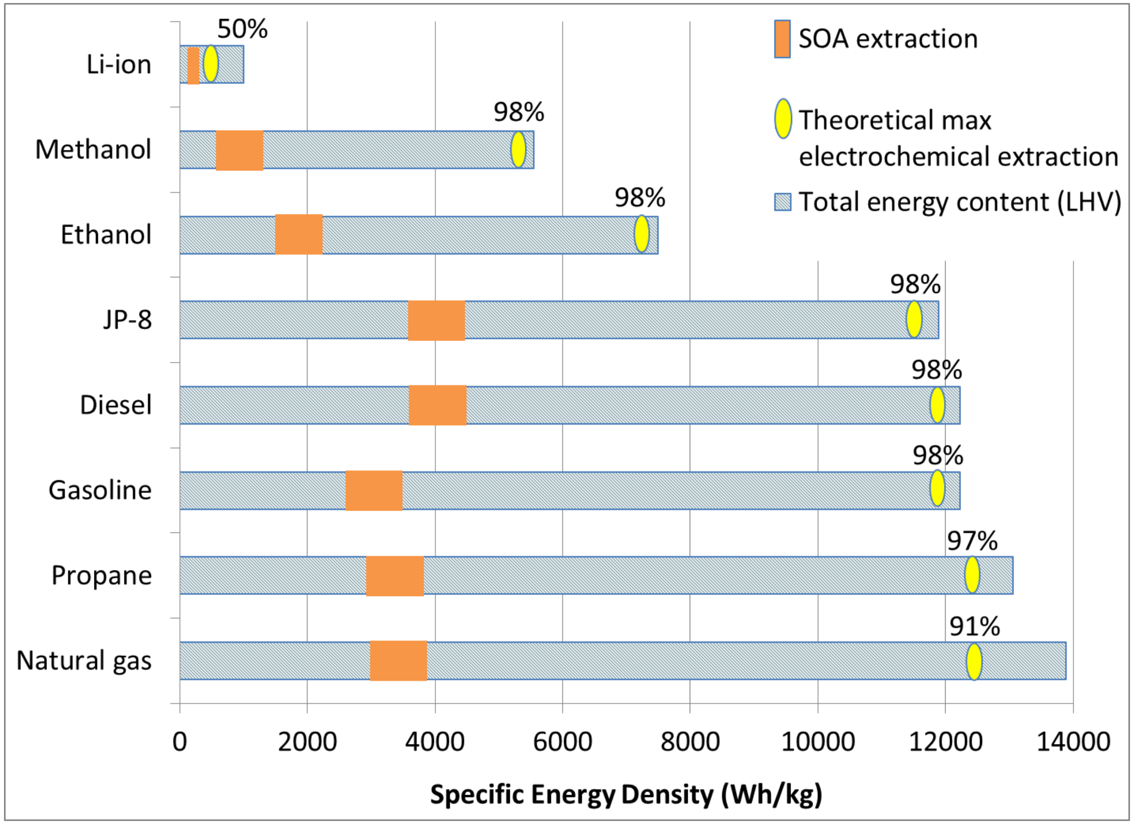
DARPA funded, fuel cell powered UAV (22 lbs).
Photo courtesy of Lockheed Martin.

DARPA funded, fuel cell powered UAV (22 lbs).
Photo courtesy of Lockheed Martin.

Memorandum of Agreement with Marine Corps Warfighting Laboratory - purchasing two UAVs for use as an experimentation platform for communications relay/network nodes.

Increased energy density: Unlocking the full potential of hydrocarbons at low temperature

High energy density materials are not fully utilized



Path Forward: Develop technologies to better utilize long-chain hydrocarbons.

Carnot Engine: Limited by temperature; significant advances require higher operating temperature (non-starter).

Solid Oxide Fuel Cells: SOA limited by balance of plant and ability to oxidize fuel; significant advances require reformers that operate at the electrode surface or reduced overall operating temperature.

Direct Electrochemistry: SOA limited to low energy density hydrocarbons; significant advances require new catalysts to efficiently cleave C-C bonds.

If we want the energy we paid for, we need to move beyond Carnot limits.

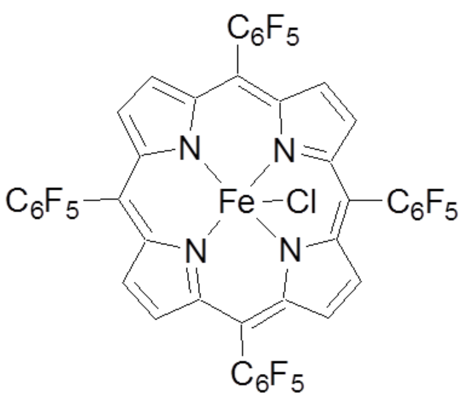
Advanced Carbon Direct Conversion (ACDC) initiatives explore new catalysts and surface structures

Experimental

ENVISIONED DEMONSTRATION: Push existing catalysts to the right conditions or place them in the proper sequence to allow deep oxidation of alkanes.

APPROACH:

- Electrochemically drive complexes used for oxidation of alkanes, ketones and esters.
- Identify new complexes for oxidative carbon-carbon bond cleavage or resulting oxidation products.



$Fe(TPPF_{20})Cl$

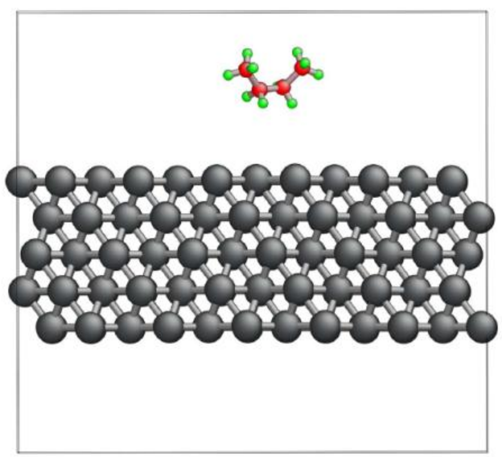
Preliminary results indicate perfluorinated iron-porphyrin can oxidize cyclohexane to cyclohexanol, cyclohexanone, and even adipic acid under mild conditions

Theoretical

ENVISIONED DEMONSTRATION: Computationally identify non-noble metal based nanostructures that will efficiently cleave C-C bonds.

APPROACH:

- Create database of parameters and possible materials critical for catalytic oxidation of alkanes.
- Develop ReaxFF model suitable for oxidation of alkanes.
- Optimize catalyst/electrolyte and nanoparticle structures.



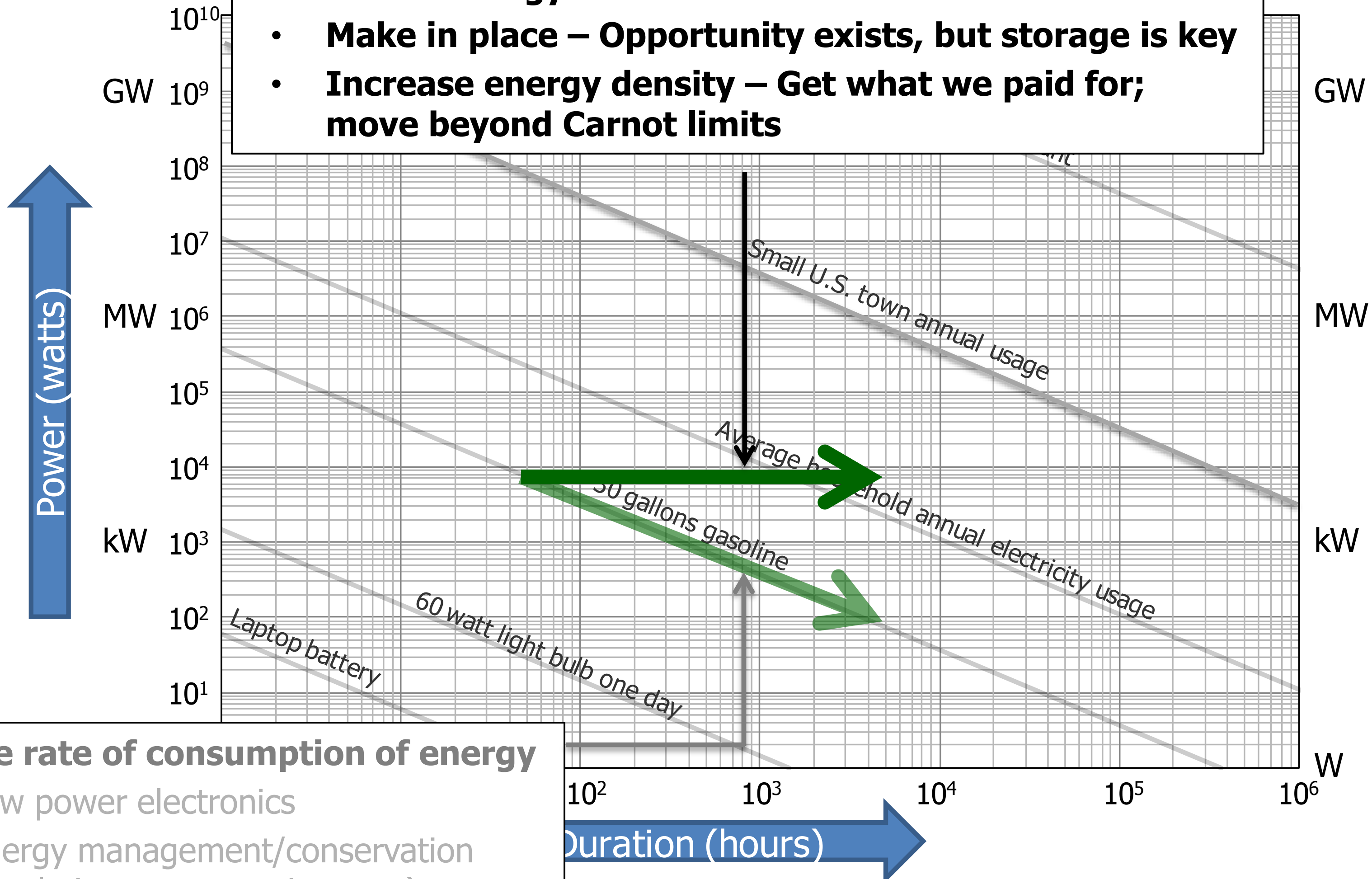
Initial work has focused on understanding the carbon-carbon bond breaking mechanism on Ni and Pt surfaces at varying temperatures to start optimization process.

Small initiatives will demonstrate feasibility of these approaches or clarify what challenges remain – significantly reducing risk of a full program.

Two options may be more feasible for DoD operations

Make more energy available

- **Make in place – Opportunity exists, but storage is key**
- **Increase energy density – Get what we paid for; move beyond Carnot limits**

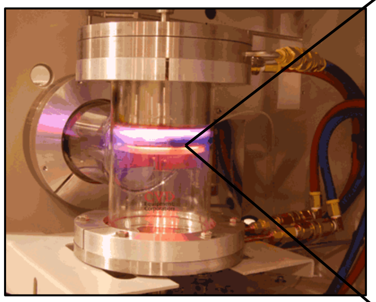


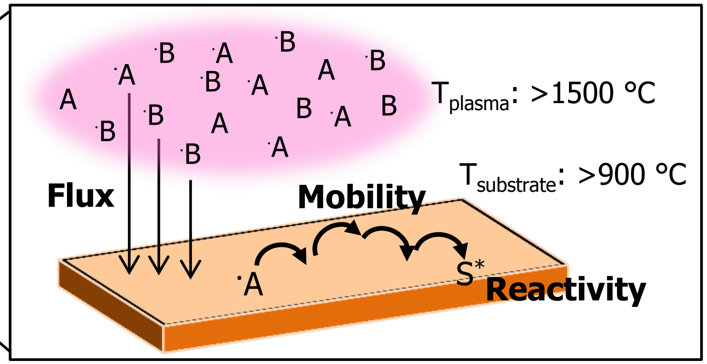
Reduce rate of consumption of energy

- Low power electronics
- Energy management/conservation (insulation, cogeneration, etc.)

Next Idea:
Local Control (LoCo) for Thin Film Synthesis

Problem: SOA thin-film deposition often requires high temperature.





CVD reactions require external energy input (E_i) to achieve critical components of thin film growth:

- **Reactant Flux (J_i)**: Creation of energetic reactants with high flux to the surface.
- **Surface Mobility (D)**: Diffusion of reactive species across the surface to reactive sites.
- **Reaction Energy (E_a)**: Achieving sufficient energy to overcome activation barriers.

In state-of-the-art (SOA) CVD, high processing temperatures are used to achieve the required energy for flux, mobility, and reaction energy.

Reactant flux:	Surface mobility:	Reaction energy:
$J_i = {}^1/_4\, n\sqrt{{}^{8\boldsymbol{E_F}}/_{\pi m}}$	$D = D_o e^{\left({}^{-E_d}/_{\boldsymbol{E_M}}\right)}$	$E_a = -\boldsymbol{E_R}\ln\left({}^{k}/_{A}\right)$
For SOA: $E_{Flux} = k_b \boldsymbol{T_{plasma}}$	For SOA: $E_{Mobility} = k_b \boldsymbol{T_{surface}}$	For SOA: $E_{Reactants} = k_b \boldsymbol{T_{reactants}}$

n = molec. conc.; m = molec. mass; Z = collisional freq; E_d = diffusional energy barrier; D_o, A = pre-exponential factor; k_b = Boltzmann constant

The result is that CVD deposition temperatures are higher than many relevant substrates can withstand

Graph illustrates that:

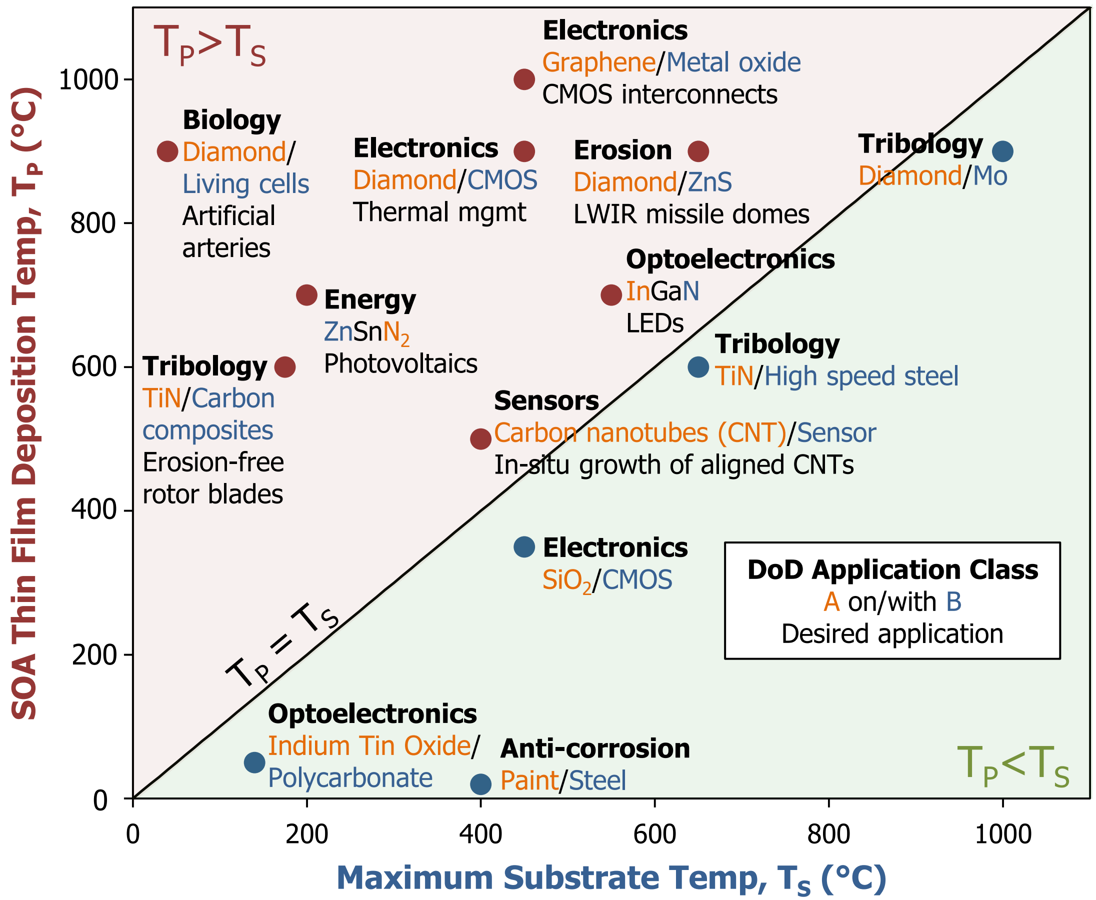
- The temperature required to deposit a coating of interest (**T_P**) is often higher than the max T a substrate can withstand (**T_S**).

$T_P=T_S$: Line of equi-temperature.

- Example coating/substrate combinations below $T_P=T_S$ are possible with SOA deposition techniques (**$T_P<T_S$**).
- Example high-value coating/substrate combinations above $T_P=T_S$ cannot be synthesized today (**$T_P>T_S$**).

T_S is defined by a material's physical properties and cannot be changed.

T_P is the bulk thermal energy used in SOA CVD techniques to achieve the required flux, mobility, and reactivity.



<u>LoCo vision</u>: Energetic requirements for flux, mobility and reactivity can be met without bulk heating. $E_{LoCo} \neq k_b T$

The new insight is that flux, mobility and reactivity really depend on ENERGY, not temperature

New insight: Non-thermal energy can provide additional control parameters for thin film deposition reactions.

Reactant flux: Raise pressure to increase n at lower T_{Plasma}

$$J_i = {}^1\!/_4\, \boldsymbol{n} \sqrt{{}^{8\boldsymbol{E_F}}\!/_{\pi m}}$$

$$\boldsymbol{n} \propto \boldsymbol{P},\; E_{Flux} = k_b T_{plasma}$$

Surface mobility: Increase energy of surface phonons.

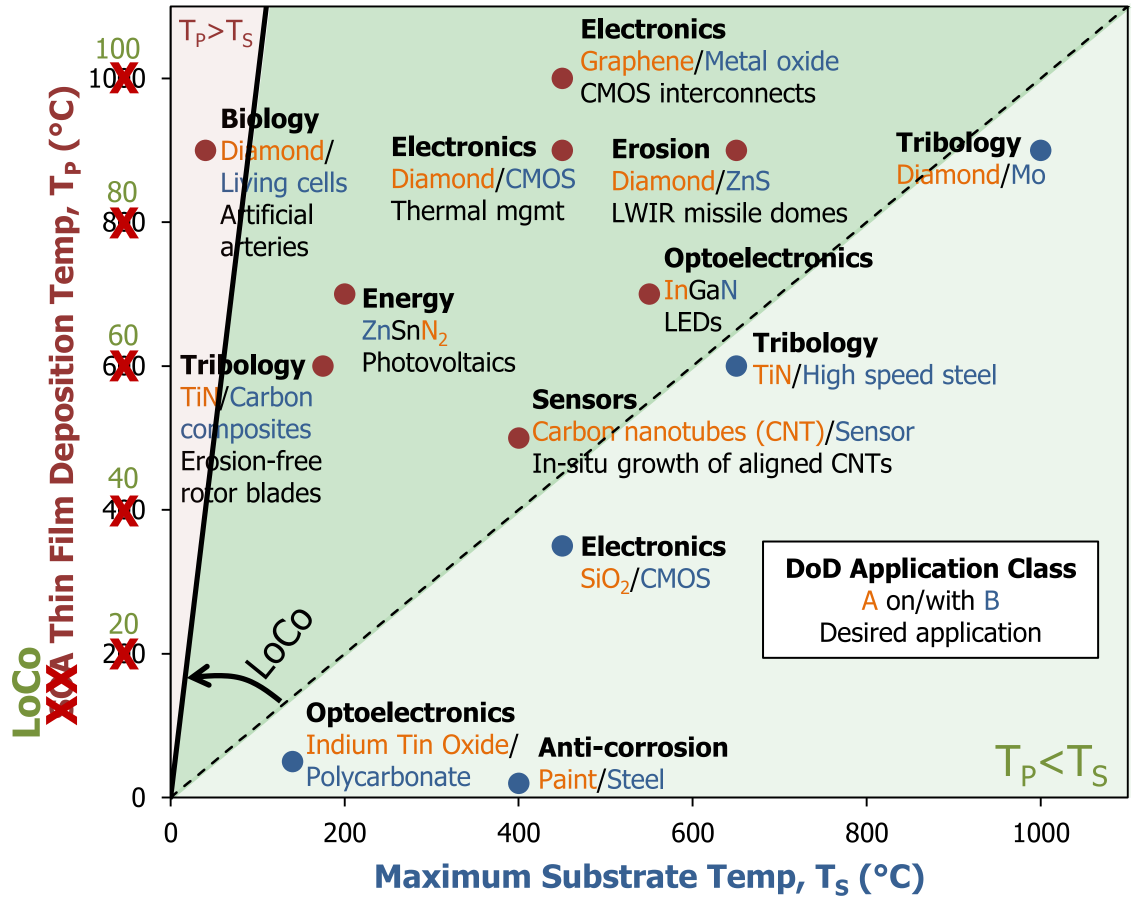
$$D = D_o e^{\left({}^{-E_d}/_{\boldsymbol{E_M}}\right)}$$

$$E_{Mobility} = (k_b T_{surface} + \boldsymbol{E_{phonon}})$$

Reaction energy: Add energy directly to bonds with photons.

$$E_a = -\boldsymbol{E_R} \ln({}^{k}/_{A})$$

$$E_{Reactants} = (k_b T_{reactants} + \boldsymbol{E_{photon}})$$



LoCo will develop non-thermal means to meet the energy needs of the deposition process

- Deposit thin films below 100 °C.
- Expand the region of addressable coating/substrate combinations.

Working with DARPA: office based initiatives

Potential Performers
Industry, Universities,
National Labs

→ **Program Manager**
Scientist
Entrepreneur

→ **Office Director**
Scientist
"Angel Investor"

→ **Office Initiatives**
(Proof of Concept)

Office Initiative →
Customer Request →
New Idea (from PM, Performer, etc) →

Step I
- Define Program Goals and Metrics
- Permission to Issue BAA – DARPA Director (Scientist, "VC")

→ **BAA**

Step II
- Proposers Day
- White Papers
- Proposal Review
- Select Performers

→ **Contract**

Step III
- Program Reviews
- "Decision Point" Evaluations
- DoD transition partners

6 months | **12 months** | **18 months** | **54-60 months**

Idea Development
- *Office Initiative*
- *RFI*
- *Workshop*

- *Pitch to Director*
- *BAA Issued*
- *Proposers Day*

- *Journal Publications from OBI's*
- *Program Phase I Underway*

Deliverables
- *Publications*
- *Transition*

www.darpa.mil